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Anion Exchange Selectivity in Water–Dioxane Medium*

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Abstract

A systematic study of the exchange behavior of the simple monovalent anions ClO_4^-, I^-, CNS^-, and Cl^- as a function of the water–dioxane solvent compositions 0, 20, 45, 70, and 82% w/w at 303 ± 0.1 °K on strong base anion exchangers such as Dowex 1-X1, Dowex 1-X2, and Dowex 1-X4 as well as on two weak base anion exchange resins (Dowex-3 and Amberlyst A-21) was carried out. The results are analyzed in terms of models proposed by Diamond and Reichenberg. The results agree qualitatively with the above models but fail to provide quantitative agreement.

INTRODUCTION

The application of ion-exchange principles to effect difficult separations and other industrial uses has far outstripped our understanding of the mechanism of the ion exchange itself (*1–3*).

The profound influence of water-soluble organic solvents (in the external phase) on ion-exchange reactions has been recognized and applied in a variety of ways. However, systematic studies of simple anions in these mixed solvents are sparse. Following the work of Diamond et al. (*4–6*) and Bhat (*7*), ion-exchange equilibria among a few simple inorganic anions in water–dioxane mixed medium were investigated with a view to learning the influence of water-soluble aprotic dioxane. The exchange studies were

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*Based on the thesis submitted by C. S. Narke to Karnatak University, Dharwad, India, for the Ph.D. degree.

made with the chloride form of the resin as the reference and the monovalent ions (ClO_4^-, I^-, CNS^-) as the counterions.

The exchange behavior of these three counterions versus the chloride was investigated as a function of the water–dioxane solvent compositions at 303 ± 0.1 °K on strong base anion exchangers such as Dowex 1-X1, Dowex 1-X2, and Dowex 1-X4. To illustrate the possible effect of the nature of the fixed co-ions on the resin, the selectivity coefficients of perchlorate versus chloride on weak base exchangers such as Dowex-3 and Amberlyst A-21 were studied. The results are discussed in terms of the models proposed by Reichenberg (*8*) and Diamond (*5*).

EXPERIMENTAL

Ion-Exchange Resins

Dowex 1-X1, Dowex 1-X2, and Dowex 1-X4 (A.R. grade, J. T. Baker Chemical Co., 50–100 mesh beads) were first conditioned in a column by alternating large excesses of 0.5 *M* sodium hydroxide and 1.0 *M* hydrochloric acid. The resin beads were converted into the chloride form by hydrochloric acid and washed free from chloride. The air-dried conditioned chloride form resin beads were stored in a stoppered polyethylene bottle until needed. The moisture content of these beads was determined in a separate experiment by carefully drying at 330 ± 1 °K. An average value of 20 ± 1 wt-% was obtained for these resins.

The specific capacity of these resins was determined by eluting a known weight of them with a large excess of 2 *M* KNO_3 and determining the displaced chloride by Volhard's method. The average capacity for all three types of resins was found to be 3.5 ± 0.2 meq/g of air-dried resins.

The weak base anion exchangers Dowex-3 (20–50 mesh) and Amberlyst A-21 (16–20 mesh), conditioned in the same manner, were converted into the OH-form and air-dried before storing. Their specific capacities were determined indirectly by the graphical extrapolation method and were found to be 4.2 ± 0.2 and 4.1 ± 0.2 meq/g of air-dried resins, respectively.

Solvents and Other Reagents

All the chemicals used were of analytical grade. Analytical grade 1,4-dioxane was further refluxed over sodium metal and freshly distilled before use. The solvent mixtures containing 20, 45, 70, and 82% w/w of dioxane were prepared by mixing the appropriate amounts of dioxane and water.

The standard solutions of various salts were usually prepared by dissolving the weighed amounts of the corresponding salts in the appropriate solvent except in the case of solutions with 82% dioxane–water mixtures. In this case the requisite quantity of the salt was first dissolved completely in a small but known amount of water followed by the addition of sufficient dioxane to give the solvent composition of 82% dioxane and 18% water. The solution thus prepared was further diluted as required by adding the water–dioxane mixed solvent of the same composition.

All the weighings were done on a Mettler B-6 balance to a precision of 0.2 mg. The composition of the solution phase after each equilibration was determined by a suitable volumetric method.

Determination of Selectivity Coefficient

In each experiment a known amount of the air-dried resin beads was placed in a stoppered flask. Measured volumes of the prepared salt solutions of 0.05 *M* were added in different proportions. These flasks were stoppered and shaken in a water thermostat maintained at 303 ± 0.1 °K for about 12 hr. In a separate experiment it was established that shaking for about 5 hr was sufficient for equilibration even for the slowest exchange rate involving 82% dioxane–water solutions. After equilibration, aliquots of solutions were pipetted out and the concentrations of the ions were determined by appropriate volumetric techniques. These data, together with the previously determined capacity of the resin, were used to evaluate the selectivity coefficient $K_{cX}{}^{Y}$ for each loading. The values of $K_{cX}{}^{Y}$ at different loadings, from 0.2 to 0.8 mole fraction of the resin phase, were thus determined. Potassium or sodium was used as the common co-ion with the strong base anion exchangers, and hydrogen ion was the common co-ion for the weak base anion exchangers. Further details of the experimental procedures were presented earlier (*9*).

RESULTS AND DISCUSSION

Considering the ion exchange reaction

$$\mathrm{RX} + \mathrm{MY}_{\mathrm{aq}} \rightleftharpoons \mathrm{RY} + \mathrm{MX}_{\mathrm{aq}} \qquad (1)$$

as a thermodynamic equilibrium, one can write the following expression for the equilibrium constant, after Gaines and Thomas (*10*):

$$\ln K_{aX}{}^{Y} = \int_{0}^{1} \ln K'_{aX}{}^{Y}\, d\bar{N}_{RY} - \int_{a_w(\bar{N}_{RY}=1)}^{a_w(\bar{N}_{RX}=1)} n_w\, d\ln a_w$$

$$- \int_{a_w=1\ (\bar{N}_{RY}=1)}^{a_w(\bar{N}_{RY}=1)} n_w d\ln a_w + \int_{a_w=1\ (\bar{N}_{RX}=1)}^{a_w(\bar{N}_{RX}=1)} n_w d\ln a_w \qquad (2)$$

where $K'_{aX}{}^{Y}$ is the corrected and averaged selectivity coefficient, n_w is the number of moles of water associated with one equivalent of exchanger, the a_w's are the corresponding activities of water, and $\bar{N}_{RY}$ and $\bar{N}_{RX}$ are the equivalent fractions of RY and RX resin forms, respectively.

The experimentally determined selectivity coefficients $K_{cX}{}^{Y}$ at a number of selected values of $\bar{N}_{RY}$ were fitted into a quadratic least-squares expression, and the average selectivity coefficient $K'_{cX}{}^{Y}$ for each pair of exchanging counterions was computed using a BESM-6 computer. The corrections for the activity coefficient ratios $(f^{\circ}_{\pm MX}/f^{\circ}_{\pm MY})$ for the external solution phase were calculated by the method of Robinson and Stokes (*11*), and the corresponding corrected and averaged selectivity coefficients $K'_{aX}{}^{Y}$ were evaluated using the following approximate equation:

$$\log K'_{aX}{}^{Y} = \int_{0}^{1} \log K_{cX}{}^{Y}\, d\bar{N}_{RY} + 2\log(f^{\circ}_{\pm MX}/f^{\circ}_{\pm MY}) \qquad (3)$$

where $f^{\circ}_{\pm MX}$ and $f^{\circ}_{\pm MY}$ are the mean molal activity coefficients of the electrolytes MX and MY, respectively, when they are present alone in aqueous solution at a given molality.

The presently available data to evaluate the remaining three integrals, viz., the 2nd, 3rd and 4th in Eq. (2), are so sparse that these corrections were not applied in all cases. In addition, the corrections for the 2nd, 3rd, and 4th integrals of Eq. (2) are insignificant, as shown below.

$$\log K_{aCl}{}^{I} = 0.900 - 0.0002 - 0.007 + 0.009$$

$$= 0.9018$$

The averaged and corrected selectivity coefficients $K_{aX}{}^{Y}$ in an aqueous medium for different systems are summarized in Table 1.

In dioxane–water mixed solvent, Eq. (3) is modified to take account of the change of the solvent nature. It can be represented by

$$\log K'_{aX}{}^{Y} = \int_{0}^{1} \log K_{cX}{}^{Y}\, d\bar{N}_{RY} + 2\log(f_{\pm MX}/f_{\pm MY}) + \log Q' \qquad (4)$$

$$= \log K''_{aX}{}^{Y} + \log Q' \qquad (5)$$

TABLE 1

Corrected and Averaged Selectivity Coefficient $K'_{a\mathrm{Cl}}{}^{\mathrm{Y}}$ in Aqueous Medium (total ionic strength, 0.05)

Resin	log $K'_{a\mathrm{Cl}}{}^{\mathrm{I}}$	log $K'_{a\mathrm{Cl}}{}^{\mathrm{CNS}}$	log $K'_{a\mathrm{Cl}}{}^{\mathrm{ClO_4}}$
Dowex 1-X4	0.90	0.96	1.64
Dowex 1-X2	0.91	0.80	1.62
Dowex 1-X1	0.68	0.93	1.64
Dowex-3	—	—	0.38
Amberlyst A-21	—	—	0.82

where Q' involves solvent activity terms and activity coefficient corrections for the difference in the standard states of the resin and the external solution phase (*12*). The first term on the right-hand side of Eq. (4) was computed as for an aqueous medium; for the second term the activity coefficient ratio of the two counterions in dioxane-water medium was taken as equivalent to the one in aqueous medium per Harned's second rule (*13*). Due to a paucity of data, the value of Q' was not evaluated. The averaged and corrected selectivity coefficients log $K''_{a\mathrm{Cl}}{}^{\mathrm{Y}}$ in dioxane-water media thus computed are summarized in Table 2.

As can be seen from Table 1, the order of selectivity of the three strong

TABLE 2

Averaged and Corrected Selectivity Coefficients ($K''_{a\mathrm{Cl}}{}^{\mathrm{Y}}$) in Dioxane-Water Medium at 303.0 ± 0.1°K

Exchanging ion	Exchanger	log $K''_{a\mathrm{Cl}}{}^{\mathrm{Y}}$ at % (dioxane w/w)			
		20.0	45.0	70.0	82.0
I^-	Dowex 1-X4	0.58	0.39[a]	0.17	0.01
	Dowex 1-X2	0.67	0.37	0.24	0.22
	Dowex 1-X1	0.74	0.47	−0.12	−0.32
CNS^-	Dowex 1-X4	0.81	0.48[a]	0.10	−0.15
	Dowex 1-X2	0.71	0.41	0.01	−0.03
	Dowex 1-X1	0.80	0.38	0.20	−0.23
ClO_4^-	Dowex 1-X4	1.29	1.15[a]	0.51	0.06
	Dowex 1-X2	1.43	0.91	0.34	0.15
	Dowex 1-X1	1.15	0.80	0.11	−0.08
	Dowex-3	0.02	−0.28	−1.20	−1.49
	Amberlyst A-21	0.66	0.39	−0.27	—

[a] The dioxane content is 40% (w/w) instead of 45% (w/w).

base exchangers (Dowex 1-X4, Dowex 1-X2, and Dowex 1-X1) in the aqueous medium is the same, viz., $ClO_4^- > CNS^- > I^- > Cl^-$, and is in good agreement with the order of the selectivities (1.98, 1.38, and 1.13) obtained by Bhat (*7*) on Dowex 1-X8 at 0.1 *M* ionic strength and with that of Jensen and Diamond (*14*) for $I^- > Cl^-$. However, a quantitative comparison among the three is not feasible because of finite differences in the experimental details. Bhat's measurements were on Dowex 1-X8 at an ionic strength of 0.1 *M*, and those of Diamond and Jensen (*14*) were by tracer anions. This observation in the aqueous medium supports the model developed by Diamond (*5*). Among the four counterions, the Cl^- ion in water at the dilution employed in the present work exhibits the highest hydration energy (*15*), and is shown in Table 3.

According to Diamond's model, the smaller anion would be in the external aqueous phase, and this is in excellent agreement with the observed selectivity order. For still larger monovalent ions such as ClO_4^- and ReO_4^-, this model suggests that selectivity is further enhanced by the entropy effect (*16*), i.e., these large anions tend to tighten up the water structure surrounding them in the same way as do hydrophobic molecules. This expectation is borne out in our experiment where $K'_{aCl}{}^{Y}$ for ClO_4^- is nearly a log unit larger than for I^- (Table 1).

Though the difference between the free energy of hydration and the standard free energy change of the ion exchange reaction shows a similar qualitative trend, quantitatively the difference is large (Table 3). This

TABLE 3

$\Delta G^\circ_{i(h)}$ of Monovalent Anions and $\Delta G^\circ_{Cl'}{}^{Y'}$ Values for Exchangers on Strong Base Exchangers at 303.0°K

Anion	Free energy of hydration ($-\Delta G^\circ_{i(h)}$) in kcal/mole	Difference between free energies of hydration ($\Delta G^\circ_{Cl'(h)} - \Delta G^\circ_{Y'(h)}$) in kcal/mole	Standard free energy change of an ion-exchange reaction ($\Delta G^\circ_{Cl'}{}^{Y'}$) in kcal/mole		
Cl^-	79	0.0	0.00		
Br^-	72	− 7	−0.57 (*15*)		
I^-	64	−15	−1.51[b]	−1.54 (7)	−1.26[c]
NO_3^-	69	−10	−0.75[b]	−0.72 (7)	
CNS^-	(55)[a]	−24	−1.63[b]	−1.88 (7)	−1.34[c]
ClO_4^-	50	−29	−2.35[b]	−2.69 (7)	−2.29[c]

[a] Estimated.

[b] K. Gartner, *Phys. Chem.* (*Leipzig*), *223*, 132 (1963).

[c] Present work.

suggests that even in aqueous media, the mechanism of ion exchange may not be as simple as assumed in Diamond's model.

In the case of two weak base anion exchangers (Dowex-3 and Amberlyst A-21), the average selectivity coefficients for the preferred ClO_4^- ion are considerably smaller, indicating a possible bonding type of interaction.

Adding dioxane to the aqueous solution generally decreases the average selectivity coefficients $K'^{Y}_{a\mathrm{X}}$ for all three pairs of ions investigated: ClO_4^-–Cl^-, CNS^-–Cl^-, and I^-–Cl^-. This reduction is largest in ClO_4^-–Cl^- and smallest in I^-–Cl^- (Figs. 1–3). In fact, there is a crossover in the selectivity order between CNS^- and I^- at around 55% dioxane–water composition.

The actual solvent composition at equilibrium may not be the same as the initial composition. In fact, Jensen and Diamond (*14*) reported that up to an external solution dioxane mole fraction of 0.8, the resin phase mole fraction is only 1/2 to 1/3 that of the external solution at equilibrium.

The partial replacement of water in the aqueous solution by dioxane apparently has three effects. First, dioxane does not possess any acidic hydrogen capable of hydrogen bonding to the anion as does the water molecule. Thus the mixed solvent will become a poorer solvating agent for anions. If we accept the single ion activity coefficient concept, then

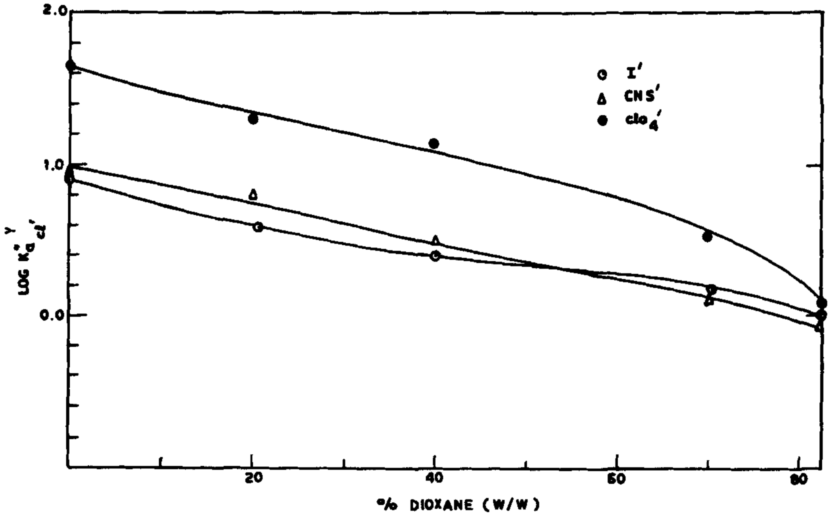

FIG. 1. Selectivity coefficients of ClO_4^-, CNS^-, and I^- as a function of dioxane–water composition on Dowex 1-X4.

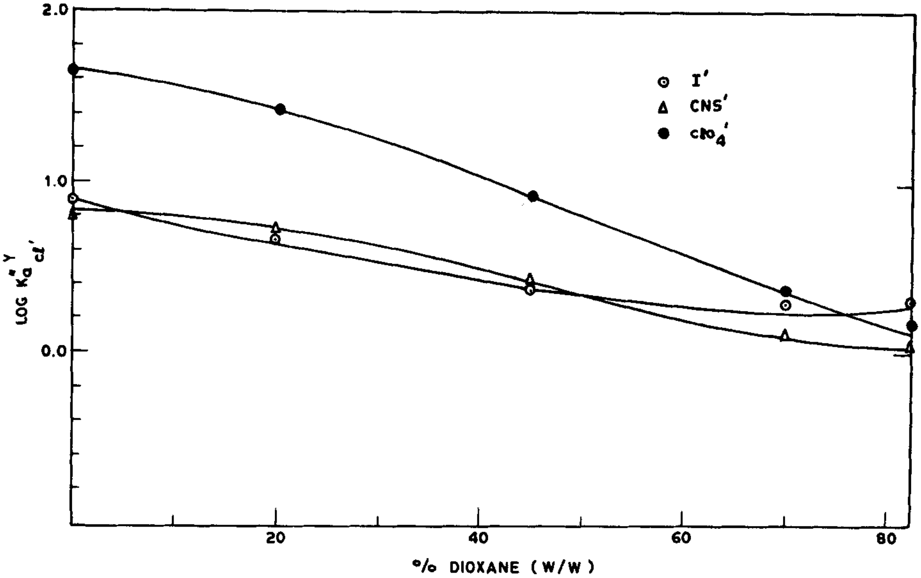

FIG. 2. Selectivity coefficients of ClO_4^-, CNS^-, and I^- as a function of dioxane–water composition on Dowex 1-X2.

these activity coefficients will increase steeply for anions with an increase in dioxane content, and more so the smaller and more basic the anion (*17*). Second, the dioxane molecule will act as a base toward the water molecules, competing with the anions for hydrogen bonding to the water and breaking up the hydrogen-bonded water structure. Finally, the addition of dioxane reduces the dielectric constant of that medium (*18*).

For these reasons the dioxane–water provides a much poorer solvating medium for the anion than does water. The effect is more marked the higher the basicity and the higher the field strength of the anions. In fact, the observation of Diamond and Jensen (*14*) that the resin phase contains a higher mole fraction of water than the external solution phase can be explained in terms of the above-mentioned effects. The resin phase with its fixed sites and mobile counterions will have a high charge density, and hence the reduction in dielectric constant on the addition of dioxane will have a much larger increase in the electrostatic free energy than the corresponding effect in the external phase. So, to keep the total free energy of a system to a minimum, water will preferentially go into the resin phase to provide electrostatic solvation. Thus the increase in dioxane con-

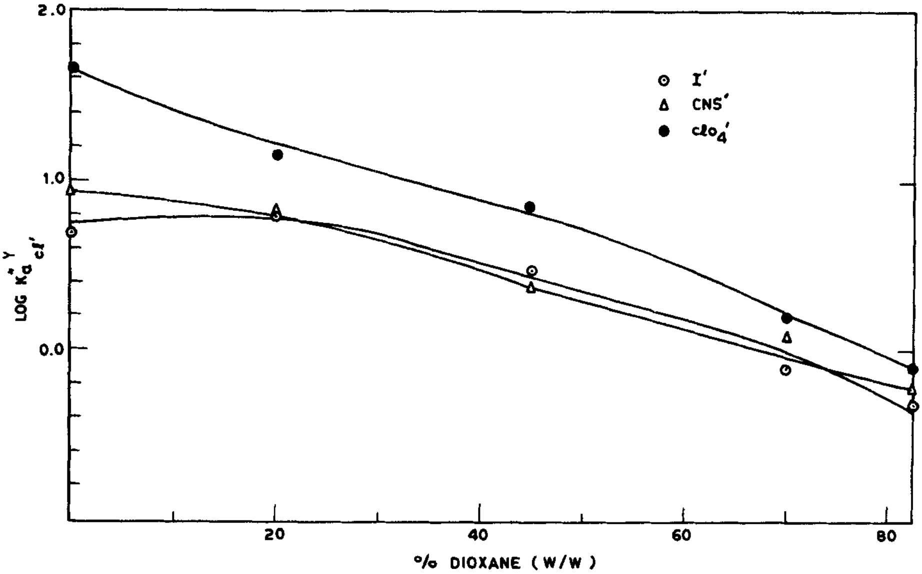

FIG. 3. Selectivity coefficients of ClO_4^-, CNS^-, and I^- as a function of dioxane–water composition on Dowex 1-X1.

centration in the total system will result in a disproportionate excess of water in the resin phase, and the superiority of the external solution over the resin phase for solvating smaller anions decreases. This explanation supports the observed decrease in the selectivity coefficient for the preferred ion in going from pure aqueous to 82% dioxane–water solvent (Table 2).

According to the model of Diamond, the preferential selectivity of ClO_4^- on the strong base resins in dioxane–water medium should decrease quite rapidly with an increase in dioxane content, both because of the reduction in superiority in the external solution for solvating Cl^- ions and the loss of water-structure-enforced ion pairing inside the resin phase. The results of the present investigation clearly support this contention (Figs. 1–3). The reduction in selectivity of CNS^- and I^- on dioxane addition is less steep because, in these two cases, the water-structure-enforced ion pairing contribution to the selectivity is less significant.

Thus dioxane addition results in reducing the relative solvation free energy change for the exchange reaction and therefore keeps a higher percentage of smaller chloride ions in the resin phase compared to the aqueous phase. In fact, on Dowex 1-X1 at the highest dioxane concentration (82%) used in the present study, Cl^- becomes the preferred ion. Thus the results observed here with strong base exchangers support the model of Diamond for the origin of selectivity as the result of the competition of the counterions for that phase which provides the best solvation, thereby minimizing the free energy of the total system. No significant effect of cross-linkage was observed for the three strong base exchangers studied for any ion pair.

It is very difficult to give a definite explanation for these observed selectivity reversals on Dowex 1-X1 at higher dioxane concentrations. The reversal observed could not be unequivocally established as a real one, or the reversal could be due to the nonexchange ion invasion. Jensen and Diamond (*14*) have reported a significant nonexchange ion invasion at very high dioxane content. Though we have not specifically investigated this aspect, we believe that the magnitude of this observed effect is about the same as that reported by them.

A direct quantitative comparison of the results for I^- and Cl^- in the present investigation and that of Jensen and Diamond could not be made since they give only tracer distribution D. But the selectivity order $I^- > Cl^-$, as well as the considerable reduction of selectivity of I^- with the addition of dioxane, are in excellent agreement. No other data are available in the literature concerning the exchange of simple anions in a water–dioxane medium.

The possible influence of Bjerrum-type ion pairing, particularly in low dielectric water–dioxane mixtures, on the selectivity coefficients $K'_{a\mathrm{X}}{}^{\mathrm{Y}}$ has not been considered. If this type of ion pairs formation in the external solution phase as a result of a lower dielectric constant of the mixed solvent medium was the cause of a smaller reduction in the $K'_{a\mathrm{X}}{}^{\mathrm{Y}}$ values than expected on the basis of solvation difference, changing the field strength of the fixed exchange sites of the resins by substituting a weakly basic tertiary ammonium ion for the strongly basic quarternary ammonium ion of Dowex 1 should reverse this effect.

With this in view, exchange studies of ClO_4^-–Cl^- on weakly basic exchangers (the gel-type Dowex-3 and a macroreticular resin, Amberlyst A-21) were carried out at pH 1.05. The results are summarized in Table 2 and Fig. 4. As expected, in both cases the absolute magnitudes of the averaged and corrected selectivities are smaller than the corresponding values observed on Dowex 1-X4, Dowex 1-X2, and Dowex 1-X1 for ClO_4^- vs Cl^-. In the case of Dowex-3, the selectivity decreased rather drastically after 40% dioxane. In fact, in solvents having a higher dioxane

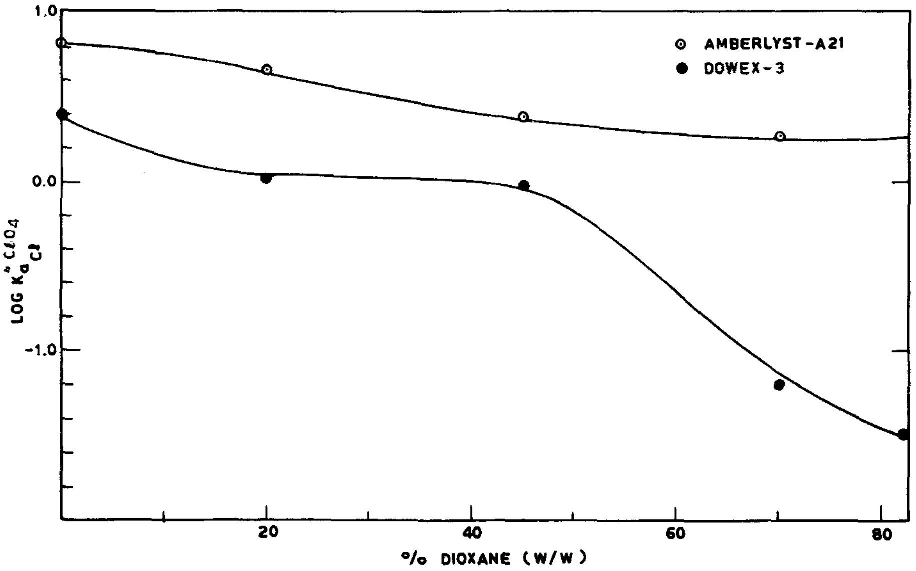

FIG. 4. Selectivity coefficient of ClO_4^- as a function of dioxane–water composition on Dowex-3 and Amberlyst A-21.

content, it is the Cl^- that is preferred, and the explanation proposed on the basis of the present model is justified.

However, the observation on Amberlyst A-21 is not so easily explainable. No doubt, the $K_{a\mathrm{Cl}}^{\mathrm{ClO}_4}$ were smaller than the corresponding ones on the strong base exchangers, but the reduction in $K_{a\mathrm{Cl}}^{\mathrm{ClO}_4}$ is smaller than expected. To what extent this can be attributed to the macroreticular pores sizes is not clear. Further work is necessary to determine this.

The results of the present anion exchange studies of ClO_4^-, I^-, CNS^-, and Cl^- in a water–dioxane medium can be explained qualitatively in terms of the models proposed by Diamond (*5*) and Reichenberg (*8*). The observed selectivity coefficient varies rather significantly with the resin phase composition both in aqueous medium and in water–dioxane solvent. As an example, the observed selectivity coefficient for the exchange of ClO_4^- vs Cl^- on Dowex 1-X1 as a function of loading is shown in Fig. 5. A satisfactory explanation as to the origin of this variation is yet to be given. A theory which can provide a quantitative description of the ion-exchange selectivity in terms of the physicochemical properties of the resin and the external solution phase is needed. Reliable exchange selec-

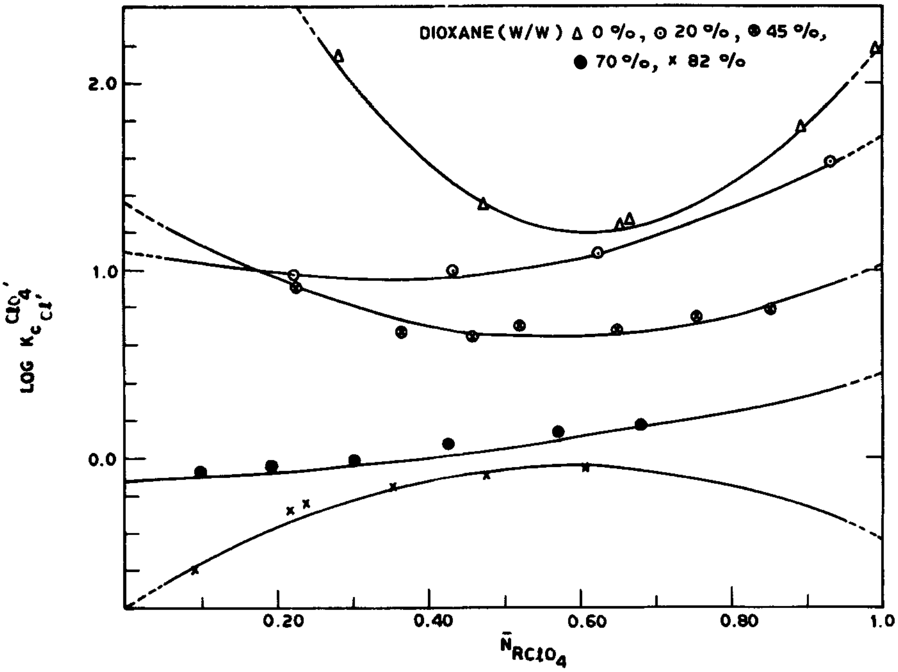

FIG. 5. Selectivity coefficient of ClO_4^- as a function of resin phase composition on Dowex 1-X1.

tivity data for well-characterized systems along with thermodynamic properties of mixed electrolyte solutions would go a long way in providing the broad base required for the evolution of such a theory.

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